Inorg. Chem. 1992, 31, 4558–4563

Effect of Alkali-Metal Cations on the Chemistry of Aqueous Silicate Solutions

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Received August 19, 1991

Silicon-29 NMR spectroscopy was used to monitor changes in aqueous alkali-metal– (M–) silicate equilibria (in solutions with $[MOH]:[Si^{IV}] \geq 1:1$) as the alkali-metal cations were complexed using cryptand 2.1.1 or 2.2.2. Peak displacements up to several ppm provide a quantitative indication of appreciable silicate–M^+ ion-pairing which decreases as the mass of M^+ is increased. The paired cations promote silicate condensation by weakening the electrostatic repulsion between anions. However, because strongly paired cations resist subsequent formation of a siloxane linkage, the level of condensation decreases systematically from M = Na to M = Cs. Paired M^+ cations demonstrably stabilize several specific oligomers by supporting their open-framework structures. Electrostrictive water-structuring by lithium ions apparently causes additional polymerization.

Introduction

Much of the research into aqueous silicate chemistry over the last decade or so has been stimulated by the goal of creating custom-tailored zeolite catalysts. This goal will not be achieved, however, until the structure-directing role exerted by cations in the zeolite synthesis mixtures is better understood. Even small amounts of cations can significantly affect the structure, in addition to nucleation and growth rates, of synthetic silicates.[1,2] Of course, such information is no less important to understanding mechanisms of mineral formation and dissolution in nature. In the literature, three main structure-directing roles have been attributed specifically to the alkali-metal M^+ cations. First, M^+ cations influence aqueous (alumino)silicate equilibria to stabilize oligomeric, "mineral-precursor" species.[3,4] Although numerous silicate[5–7] and aluminosilicate[8,9] oligomers indeed exist in solution, it is now recognized that they are exceedingly labile under conditions of mineral formation[8,10] and, unless stabilized, are unlikely to affect crystal structure directly.[11] Second, hydrated M^+ cations have a "templating" effect whereby silicate or aluminate species replace waters of hydration sufficiently long that they become bound together within a structural configuration, at or near the crystal surface, that is maintained during crystal nucleation and growth.[1,2] Although there is evidence to suggest that hydrated tetraalkylammonium cations act this way,[1] none exists to indicate convincingly that alkali-metal cations function as templates. A third hypothesis originated from recent NMR findings that (i) the extent of condensation in alkali-metal silicate solutions increases slightly as the mass of M^+ is increased[7,12] and (ii) M^+ cations form ion-pairs with silicate anions.[13,14] It was suggested, therefore, that higher silicate oligomers are favored because of preferential ion-pair formation with heavier cations.[4,7,14] The implication was that silicate–M^+ ion-pairing could similarly stabilize structural elements during stages of mineral nucleation and growth.

The objective of the present study was to employ ^{29}Si NMR to monitor changes in aqueous M–silicate equilibria as alkali-metal cations are complexed by cryptands. The findings reveal the particular importance of silicate–M^+ ion-pairing.

Experimental Section

Silicate solutions were prepared by dissolving amorphous silica, obtained either by hydrolysis of redistilled $SiCl_4$ (Aldrich, 99.999%) or as 95% ^{29}Si-enriched SiO_2 (U.S. Services), in standardized aqueous MOH solutions.[7,8] In all cases, the solvent was 20% isotopically enriched in deuterium to provide an internal NMR lock. Hydroxide solutions were prepared from $LiOH{\cdot}H_2O$ (99.95%), NaOH, KOH (both 99.99%), RbOH, CsOH (both 99.9% in 50 wt % aqueous solution), or tetra-*n*-butylammonium hydroxide (40 wt % aqueous solution) (all Aldrich). In order to minimize contamination from adventitious metal ions, solutions were permitted contact only with surfaces of low-density polyethylene and Teflon FEP/TFE which had been soaked in successive dilute solutions of nitric acid, hydrochloric acid, and Na_2H_2EDTA.

Cation Complexation. To determine the extent and consequence of silicate–M^+ interactions in solution, alkali-metal cations were complexed in situ using the macrobicyclic diamines "cryptand 2.1.1", $[N(CH_2CH_2OCH_2CH_2OCH_2CH_2)(CH_2CH_2OCH_2CH_2)_2N]$, and "cryptand 2.2.2", $[N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N]$.[15] Cryptand 2.1.1 forms a highly stable 1:1 complex in water with Li^+ ($\log K = 5.5$) whereas the larger 2.2.2 ligand associates most readily with K^+, Rb^+, and Na^+ ($\log K = 5.4$, 4.4, and 3.9, respectively) owing to, in each case, a favorable size correlation between the cation and central ligand cavity.[16] Because of the inclusive conformation of these complexes (i.e., endo-endo configuration of the bridgehead nitrogens), the encrypted cation is completely desolvated and thereby excluded from interaction with silicate ions.

Cryptands 2.1.1 and 2.2.2 (both Aldrich, 98%; none of 27 potential contaminants detectable by ICP) were added under nitrogen to silicate solutions containing Li^+ and containing Na^+, K^+, Rb^+ or Cs^+, respectively. NMR data revealed that, in the cases of Na^+ and Rb^+, ca. 5–10% excess cryptand 2.2.2 was generally required to ensure optimum complexation. As expected, the comparatively large Cs^+ cation did not readily associate with added cryptand 2.2.2 ligand.

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(1) Barrer, R. M. *Hydrothermal Chemistry of Zeolites*; Academic Press: London, 1982. Barrer, R. M. In *Zeolite Synthesis*; Occelli, M. L., Robson, H. E., Eds.; ACS Symposium Series, No. 398; American Chemical Society: Washington, DC, 1989; p 11.

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(3) Barrer, R. M. *Chem. Br.* **1966**, 380.

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(5) Harris, R. K.; Knight, C. T. G. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 1525, 1539; *J. Mol. Struct.* **1982**, *78*, 273; *J. Am. Chem. Soc.* **1981**, *103*, 1577.

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(7) Kinrade, S. D.; Swaddle, T. W. *Inorg. Chem.* **1988**, *27*, 4253.

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(9) Mortlock, R. F.; Bell, A. T.; Radke, C. J. *J. Phys. Chem.* **1991**, *95*, 372.

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(11) Knight, C. T. G. *Zeolites* **1990**, *10*, 140.

(12) McCormick, A. V.; Bell, A. T.; Radke, C. J. In *Perspectives in Molecular Sieve Science*; Flank, W. H., Ed.; ACS Symposium Series, No. 368; American Chemical Society: Washington, DC, 1988; p 222.

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(14) McCormick, A. V.; Bell, A. T.; Radke, C. J. *J. Phys. Chem.* **1989**, *93*, 1733, 1737.

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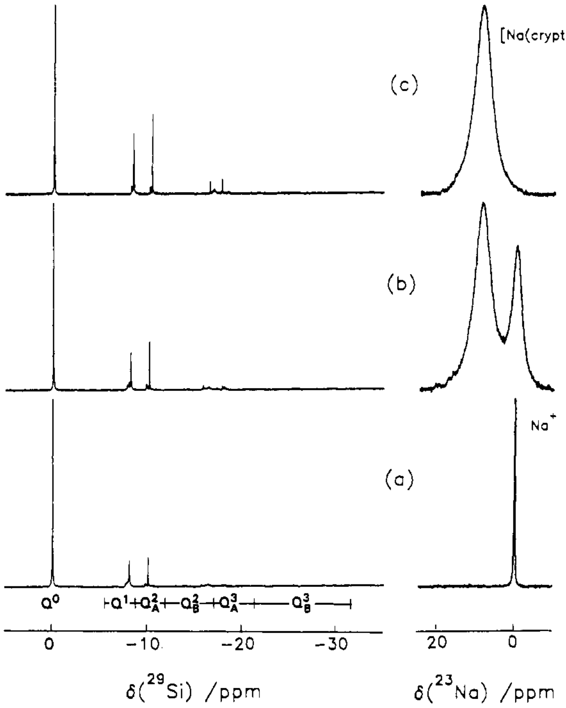

Figure 1. ^{29}Si (39.7 MHz) and ^{23}Na (52.9 MHz) spectra at 279 K of sodium silicate solutions with 0.28 mol kg^{-1} SiO_2 (95% ^{29}Si-enriched), 1.4 mol kg^{-1} NaOH, and (a) 0, (b) 1.0, and (c) 1.6 mol kg^{-1} cryptand 2.2.2. Band assignments are indicated.[19]

pH measurements of representative silicate solutions were conducted using an Orion ROSS glass pH electrode with low alkali error (e.g., 0.02 pH error at 25 °C for a pH 12 solution containing 1 mol dm^{-3} Na^+) and were uncorrected.[17] For large samples (not containing cryptand) measurements were made using a double-junction reference electrode in order to minimize any liquid–liquid junction potential.

NMR measurements were performed with Bruker AC-E 200 and AMX 500 spectrometers (39.73 and 99.36 MHz, respectively, for ^{29}Si) using probehead inserts and sample tubes constructed from Si- and Al-free materials.[18] Silicon-29 90° pulses were cycled over periods greater than 3–5 times the maximum measured T_1 value to ensure quantitative spectral integration.[13] All ^{29}Si assignments are from previous studies.[5-7] The formation of $[M(cryptand)]^+$ complex was confirmed using alkali-metal NMR spectroscopy. (See e.g. Figure 1).

In accordance with established practice, the $Q^y{}_z$ symbol is used throughout this report to denote a quadrafunctional Si center with *y* connectivity (i.e., *y*-coordinated $SiO_4{}^{4-}$ tetrahedra) and, when applicable, *z* indicates the number of equivalent centers in a totally symmetric anion. ^{29}Si resonances corresponding to Q^2 and Q^3 centers are conveniently subdivided into A and B spectral regions (Figure 1).

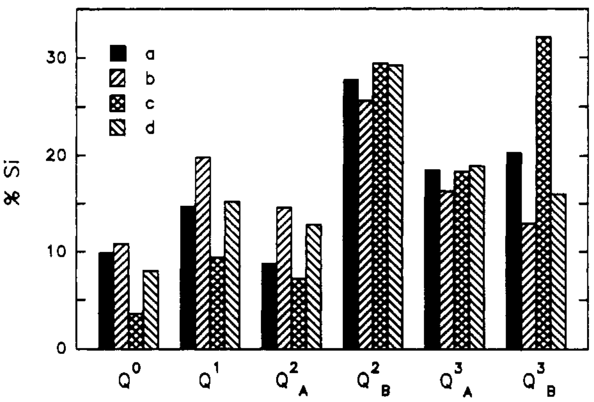

Figure 2. Distribution of Si among the different connectivity states in (a) a solution with 0.9 mol kg^{-1} SiO_2 and KOH, (b) the previous solution with additional 0.9 mol kg^{-1} cryptand 2.2.2, (c) the previous solution with additional 0.9 mol kg^{-1} KCl, and (d) the previous solution with additional 0.9 mol kg^{-1} cryptand 2.2.2.

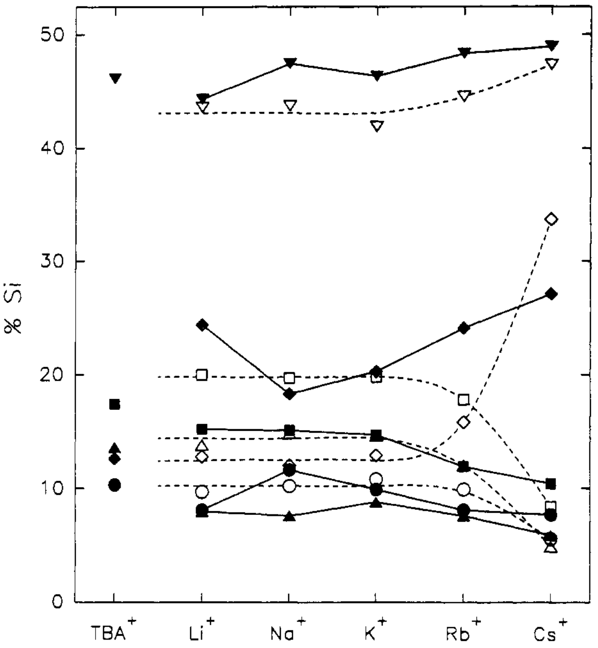

Figure 3. Influence of M^+ on the distribution of Si among different connectivity states at 300 K in solutions with 0.9 mol kg^{-1} SiO_2 and 0.9 mol kg^{-1} MOH or tetra-*n*-butylammonium (TBA^+) hydroxide: ●, Q^0; ■, Q^1; ▲, $Q^2{}_A$; ▼, $Q^2{}_B$ + $Q^3{}_A$; ◆, $Q^3{}_B$. Filled symbols and solid lines correspond to solutions containing free cations. Open symbols and broken lines correspond to solutions containing cryptand (2.1.1 in the case of Li^+ and 2.2.2 in all other cases). In the latter solutions, Li^+, Na^+, and K^+ cations were fully encrypted whereas a small fraction of Rb^+ and the bulk of Cs^+ remained uncomplexed.

Results

Equilibria. As typified in Figure 1, the proportion of ^{29}Si resonances corresponding to high-connectivity Si centers increased as cryptand was added to alkali-metal silicate solutions with concentration ratio $[OH^-]:[Si^{IV}] \gg 1:1$ and $[Si^{IV}] \gtrsim 0.1$ mol kg^{-1}. Smaller gains in the extent of silicate condensation were observed at progressively lower $[OH^-]:[Si^{IV}]$ ratios such that, at ratios approaching 1:1, cryptand addition ultimately resulted in *de*polymerization (Figure 2). Cryptand, noncomplexed M^+ cations (compare Figure 2b with Figure 2c), and $[M(cryptand)]^+$ complex (compare Figure 2a with Figure 2c and Figure 2b with Figure 2d) all favored increased silicate polymerization when present at concentrations of $\gtrsim$0.1 mol kg^{-1}. The polymerizing influence of M^+ cations rose as in the order $Na^+ < K^+ < Rb^+ < Cs^+$. However, high connectivities observed for Li silicates did not conform with this group trend (Figure 3). All differences due to the nature of M^+ disappeared once the cations were encrypted. The resulting ^{29}Si spectra contained fewer resonances and matched closely with spectra of equally concentrated (M^+ free) tetra-*n*-butylammonium silicate solutions (Figures 3 and 4). As summarized in Table I, resonances that were noticeably disfavored by M^+ complexation correspond to open-structured oligomers having acyclic appendages (e.g., substituted cyclic trimer and tetramer) or containing five-membered, or larger, silicate rings. These observations are summarized in Table I. In particular, the pentacyclic heptamer and the hexacyclic octamer

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(17) Licht, S. *Anal. Chem.* **1985**, *57*, 514.

(18) Kinrade, S. D.; Swaddle, T. W. *J. Magn. Reson.* **1988**, *77*, 569.

(19) The extreme breadth of the ^{23}Na resonance for $[M(cryptand)]^+$ arises from reduced electronic symmetry of the nucleus in this environment. In addition, rapid chemical exchange between the two ^{23}Na sites causes broadening of both resonances. In the absence of free M^+ ions, cryptand complexes are demonstrably nonlabile at the temperatures employed in this study (Ceraso, J. M.; Smith, P. B.; Landers, J. S.; Dye, J. L. *J. Phys. Chem.* **1977**, *81*, 760).

(20) Silicate anions are diagrammatically represented by stick figures in which each line corresponds to a Si–O–Si linkage. Where applicable, a dot represents a resonating Si center.

(21) Knight, C. T. G.; Kirkpatrick, R. J.; Oldfield, E. *J. Chem. Soc., Chem. Commun.* **1989**, 919.

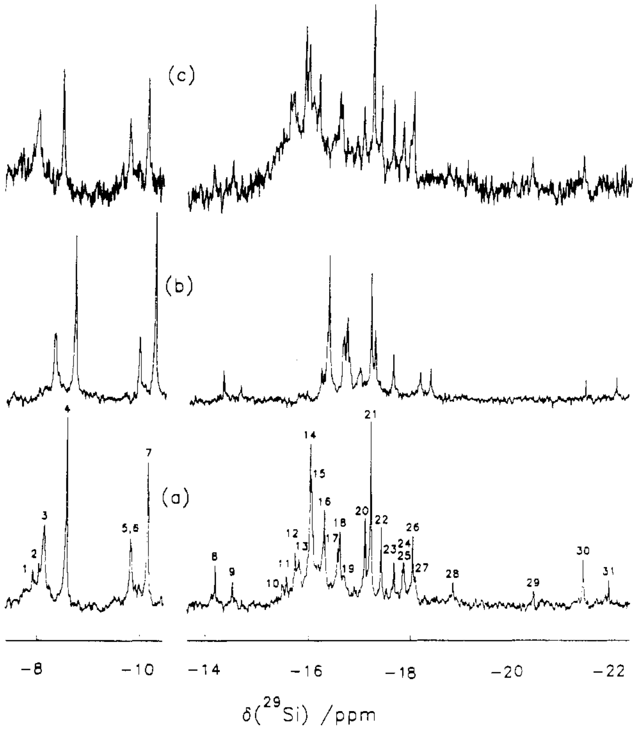

Figure 4. Expanded ^{29}Si (39.7 MHz) spectra at 300 K for solutions a–c of Figure 2. Assignments for the numbered resonances are listed in Table I and were made in accordance with refs 5 and 6. The intensity of each spectrum is normalized to its tallest peak.

could be detected *only* in solutions containing "free" M^+ ions. In highly polymerized solutions, these species occurred at the notable expense of the tetrahedral tetramer Q^3_4 and the cubic octamer Q^3_8 (Figure 5).

In accordance with the observations of McCormick et al.,[12] pH was relatively independent of the type of M^+ cation in solution. However, pH increased slightly as cryptand was added. Representative data are given in Table II.

^{29}Si Chemical Shifts. All ^{29}Si resonances moved downfrequency as the M^+ cations were encrypted. This occurred especially at low temperature, high Si^{IV} concentration, and high $[OH^-]:[Si^{IV}]$ ratios (Figure 6). The low-frequency resonances within each Q^y spectral region, i.e. corresponding to Si centers in relatively unstrained polyanions,[7] were most affected and, among these, shifts increased with silicate connectivity (Figures 6 and 7). For example, the greatest movement was of resonances corresponding to the cubic octamer Q^3_8 and tetrahedral tetramer, whereas the Q^0, Q^1, and prismatic hexamer Q^3_6 resonances were least shifted.

At ratios $[OH^-]:[Si^{IV}] > 1:1$, resonances moved to higher frequencies as the mass of M^+ was decreased. Such cation dependence increased with Si^{IV} concentration, $[OH^-]:[Si^{IV}]$ ratio, and connectivity at the resonating Si nucleus. For example, replacing Cs^+ with Na^+ at 298 K shifted the monomer Q^0 resonance upfrequency by ~0 ppm at 1.0 mol kg^{-1} Si^{IV} and $[OH^-]:[Si^{IV}] = 1:1$, 0.8 ppm at 1.0 mol kg^{-1} Si^{IV} and $[OH^-]:[Si^{IV}] = 4:1$, and 1.4 ppm at 2.0 mol kg^{-1} Si^{IV} and $[OH^-]:[Si^{IV}] = 4:1$.

At $[OH^-]:[Si^{IV}] \sim 1:1$, resonances responded differently from one another as M^+ mass was varied. For example, Figure 7 shows that the Q^3_8 peak lies furthest upfrequency with Li^+ and least with Cs^+ (0.3 ppm difference) while the Q^3_6 resonance is furthest upfrequency with Cs^+ and least with Na^+ (0.1 ppm difference). Following complexation of the alkali-metal cations, however, all ^{29}Si resonances moved downfrequency to a common series of chemical shift values (measured with respect to the Q^0 resonance) which coincided with values for an equivalent tetra-*n*-butylammonium silicate solution (Figure 7).

Finally, ^{29}Si shifts were unaffected by changes in the concentration of chloride ions, $[M(cryptand)]^+$, or free cryptand ligand (Figure 7).

Discussion

Phenomena known to affect ionic reaction systems can, in general, be divided into *electrostatic* (pertaining to the action of ionic charge on solvent and solute molecules) and *nonelectrostatic* (pertaining to the formation of solvent cavities) contributions.[22] The latter influence, i.e. that of hydrophobic nonelectrolytes, is often described using a water–clathrate analogy although its true nature remains poorly understood.[22] Nonetheless, a reasonably expected consequence would be decreased "bulk" solvent activity, which should, in turn, promote silicate condensation (via water elimination). Accordingly, soluble alcohols and amines increase the extent of silicate oligomerization without uniquely favoring or disfavoring any particular species (in the absence of tetraalkylammonium cations).[23] The free cryptand ligand and $[M(cryptand)]^+$ complex exert similar polymerizing influences which are therefore attributed to nonelectrostatic hydration. The prevalence of tetrahedral tetramer Q^3_4 and cubic octamer Q^3_8 in highly polymerized solutions containing $[M(cryptand)]^+$ (see Figure 5) indicates that the metal–cryptate complex might also play a role analogous to that of the tetramethylammonium cation.[4] Any such influence must be comparatively minor, however, since it is apparent only in highly polymerized solutions and at low alkalinity.

Dissolved alkali-metal cations are known to alter many properties of water due to electrostatic interactions; small M^+ ions are considered to be "structure-making" and larger cations to be "structure-breaking" with respect to the water lattice.[22] Although only very limited success has been achieved in quantifying the influence of solvent-structuring on reaction processes, this phenomenon has been proposed nonetheless as the primary mechanism by which cations influence silicate equilibria.[2,4] Of the alkali-metal cations, only Li^+ promotes formation of a relatively long-lived electrostrictive hydration region.[22] Indeed, this may well explain the anomalous character of lithium silicates, i.e., low solubility, high polymerization levels, and slow nuclear relaxation. However, the electrostatic interaction between larger M^+ cations and water molecules does not extend significantly beyond the tightly bound, primary hydration sphere. Moreover, since the interaction decreases from $M^+ = Na^+$ to $M^+ = Cs^+$,[22] this phenomenon can not of *itself* account for the corresponding increase in silicate condensation.

The hypothesis that polysilicate anions are stabilized by ion-pairing[4,7,12] is considered next, following examination of the influence of M^+ cations on ^{29}Si chemical shifts. Intermolecular shielding contributions can be represented by four shielding constants: van der Waals screening caused by intermolecular dispersion forces, $\sigma_{inter}{}^{V}$; the electric "reaction" field associated with each anion's hydration shell, $\sigma_{inter}{}^{E}$; direct silicate$\cdots$$H_2O$ H-bonding, $\sigma_{inter}{}^{H}$; and silicate–M^+ ion-pairing, $\sigma_{inter}{}^{IP}$.[24] At the concentrations employed in the present study, changes to $\sigma_{inter}{}^{IP}$ and $\sigma_{inter}{}^{H}$ easily predominate over the other two. Indeed, ^{29}Si chemical shifts depended neither on ionic strength nor on the presence of "free" cryptand or $[M(cryptand)]^+$ complex (Figure 7). An increase in pH is known to yield upfrequency line shifts as a consequence of silicate deprotonation, i.e., decreased local paramagnetic shielding $\sigma_{local}{}^{P}$.[7] However, resonances moved downfrequency as M^+ cations were complexed—despite the apparent increase in pH—indicating that $\sigma_{inter}{}^{IP}$ changes outstrip

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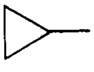
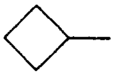
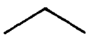
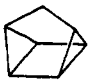
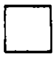
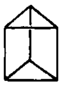
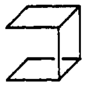
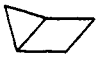
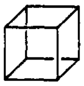
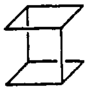
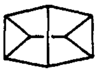
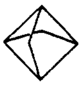
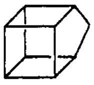
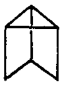
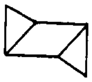
[22] Franks, F. In *Water. A Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1975; Vol. 2. Krestov, G. A. *Thermodynamics of Solvation. Solution and Dissolution*; *Ions and Solvents*; *Structure and Energetics*; Elis Horwood: New York, 1991.

[23] Kinrade, S. D.; Maa, K. J. Unpublished study.

[24] Ramsey, N. F. *Phys. Rev.* **1952**, *86*, 243. Laszlo, P. *Prog. NMR Spectrosc.* **1967**, *3*, 231. Rummens, F. H. A. *NMR* **1975**, *10*, 1. Ebraheem, K. A. K.; Webb, G. A. *Prog. NMR Spectrosc.* **1977**, *11*, 149.

Table I. Effect of Alkali-Metal Complexation on Relative Populations of Silicate Oligomers[a],[20]

Decreased abundance	Indeterminate[b] influence	Increased abundance
 substituted cyclic trimer[m] [2, 6, 27][c]	 dimer (Q^1_2) [4]	 cyclic trimer (Q^2_3)[w] [7]
 substituted cyclic tetramer[m] [1, 13]	 linear trimer [3, 19]	 tetrahedral tetramer (Q^3_4)[s]
 pentacyclic heptamer[s] [25, 28]	 cyclic tetramer (Q^2_4) [15]	 prismatic hexamer (Q^3_6)[w] [21]
 tricyclic octamer[m] [10]	 bicyclic pentamer [5, 16, 20]	 cubic octamer (Q^3_8)[s]
 tricyclic octamer[m] [11]	 bridged cyclic tetramer [8, 31]	
 hexacyclic octamer[s] [23, 29]	 double bridged cyclic tetramer [9, 30]	
 pentacyclic nonomer[m] [12, 26]	 tricyclic hexamer [14, 17, 22]	
	 tricyclic hexamer [*cis*: 18] [*trans*: 24]	

[a] List not inclusive. [b] Due to increase in overall extent of polymerization, or to uncertain line assignments. [c] Numbers correspond to peak labels in Figure 4. [s] Strong influence. [m] Moderate influence. [w] Weak influence.

Table II. pH Measurements of Representative M$^+$–Silicate Solutions[a]

M	[Si^{IV}]/mol kg^{-1}	[MOH]/mol kg^{-1}	pH no cryptand	pH 0.9 mol kg^{-1} cryptand
Na	0.90	0.90	12.92	
K	0.90	0.90	13.05	13.36
Rb	0.90	0.90	12.93	
Cs	0.90	0.90	12.92	
Na	0.90	1.8	13.62	14.10
K	3.0	3.0	14.31[b]	
Rb	3.0	3.0	14.42[b]	
Cs	3.0	3.0	14.38[b]	

[a] Include systematic pH error due to 20% ^{2}H-isotopic enrichment of solvent. [b] Measured using a reference electrode with a double junction to minimize error arising from junction potential.

all others (including the small opposing change of $\sigma_{\text{inter}}^{\text{H}}$). We conclude that alkali-metal cations induce upfrequency line shifts, which are indicative of the corresponding silicate–M$^+$ ion-pair formation constants K_{IP} (averaged over the ca. 10^{-3}–10^{-2}-s time frame of ^{29}Si NMR).

For instance, Figures 6 and 7 demonstrate that K_{IP}'s are largest for highly connected Q^3 centers in polyanions with low molecular strain (smallness of Si–O–Si bond angles[7]) such as the cubic octamer Q^3_8 and tetrahedral tetramer Q^3_4. On the other hand, ion-pair formation constants are smallest for the monomer, terminal Q^1 centers (of, e.g., the dimer, acyclic trimer, and substituted trimer) and the highly strained prismatic hexamer Q^3_6. These findings are consistent with theoretical calculations showing that the net atomic charge on silicon rises as its connectivity is increased from Q^0 to Q^3 and, for a given connectivity state, is highest for Si atoms in unstrained structural centers.[25,26] Thus, all structural factors which affect ^{29}Si chemical shift (see Tables I and II in ref 7) evidently control the extent of silicate–M$^+$ ion-pairing. ^{29}Si shift measurements further reveal that ion-pairing is favored by increased [OH$^-$]:[Si^{IV}] ratio (i.e., due to silicate deprotonation), decreased temperature, and, at high alkalinities especially, lighter alkali-metal cations (i.e., K_{IP}'s decrease as in the order Li$^+$ > Na$^+$ > K$^+$ > Rb$^+$ > Cs$^+$). This dependence on M$^+$ mass is analogous to that reported for adsorption of alkali-metal cations onto silica gel in alkaline solution.[27] A small influence of anion structure on cation selectivity can be detected at [OH$^-$]:[Si^{IV}] ~ 1:1 (Figure 7).

Employing the relationship due to Janes and Oldfield[25] which correlates ^{29}Si chemical shift with the group electronegativity of silicon substituents, we find that ion-pairing in solutions with [OH$^-$]:[Si^{IV}] = 1:1 can reduce the electronegativity of terminal hydroxy groups by more than 0.05 Pauling unit (on the basis of Na$^+$-induced displacement of the Q^3_4 resonance at 273 K). Thus, the level of Coulombic association must be substantial, even at low alkalinity, given that the electronegativity difference between the –OH and –ONa fragments of *solid* silicates is only 0.15.[25]

Circumstances favoring silicate–M$^+$ electrostatic association have been identified, but what of ion-pairing's effect on polysilicate equilibria? We have shown that alkali-metal cations yield slightly higher polymerization levels for silicates. In silicate solutions containing highly charged aluminate AlO_4^{5-} or gallate GaO_4^{5-} ions, M$^+$ cations cause polymerization so extreme that the

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(25) Janes, N.; Oldfield, E. *J. Am. Chem. Soc.* **1985**, *107*, 6769; **1986**, *108*, 5743.
(26) Englehardt, G.; Michel, D. *High-Resolution Solid-State NMR of Silicates and Zeolites*; Wiley: Chichester, U.K., 1987.
(27) Depasse, J.; Watillon, A. *J. Colloid Interface Sci.* **1970**, *33*, 43.

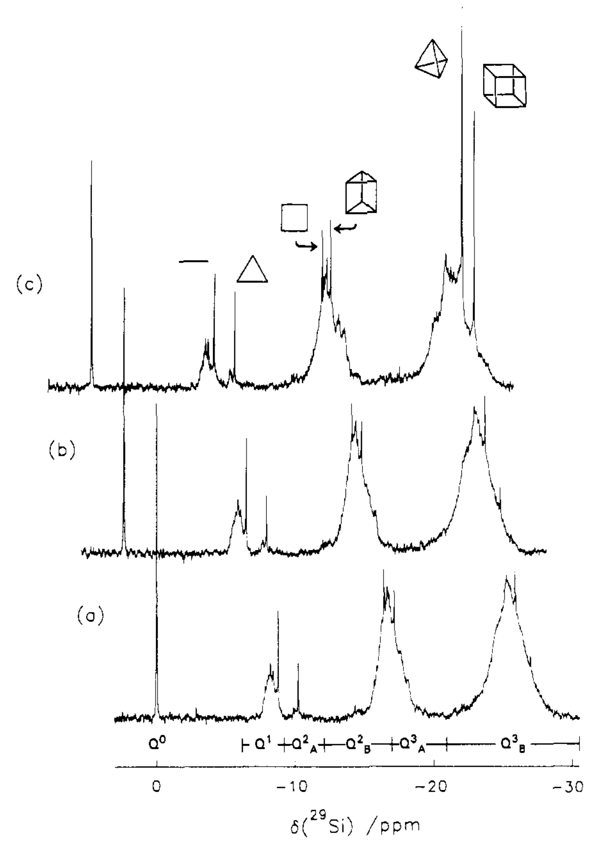

Figure 5. ^{29}Si (39.7 MHz) spectra at 274 K of a solution with 0.8 mol kg^{-1} SiO_2 (95% ^{29}Si-enriched) and NaOH, in addition to (a) 0, (b) 0.3, and (c) 1.0 mol kg^{-1} cryptand 2.2.2. Seven singlet resonances (labeled[20]) were detected in (c) by use of single-spin filtering.[21]

corresponding metallosilicate precipitates unless solutions are very dilute.[28] These observations are consistent with a reaction mechanism in which cations mediate silicate condensation by diminishing the Coulombic repulsion between anions:

$$H_3SiO_4^- \quad + \quad M^+\ldots{}^-O\text{-}Si\equiv$$

$$\rightleftarrows \qquad (1)$$

$$(HO)_3Si\text{-}O^-\ldots M^+\ldots{}^-O\text{-}Si\equiv$$

$$\rightleftarrows \qquad (2)$$

$$^-(OH)_2Si\text{-}O\text{-}Si\equiv \quad + \quad MOH$$

The extent of polymerization increases as the mass of M^+ is increased despite a corresponding decrease in ion-pair formation constants. Further, ion-pairing is negligibly affected by the size and structure of polysilicate anions, i.e., other than by factors which influence the charge of individual SiO_4^{4-} centers. (E.g., K_{IP}'s decrease as in the order $Q^3_8 > Q^2_4 > Q^1_2 > Q^3_{6}$.) Therefore, our findings do not uphold the previous hypothesis[7,12,14] that polymerization is favored by preferential ion-pairing between heavier cations and larger anions. Rather they indicate that, while paired cations promote encounters between silicate anions (eq 1), strongly paired cations hinder subsequent condensation (eq 2).

Silicate–M^+ ion-pairing also influences the stability of specific polyanions. (See Table I.) These tend to be large structures with open frameworks that, without the support of paired cations, would quickly rearrange into polyanions that are comparatively rigid and, thus, energetically preferred (e.g., tricyclic octamers → cubic octamer). This is the first demonstration of individual silicate oligomers being stabilized by alkali-metal cations and may provide some insight into the size and shape of structural elements supported by cations during mineral evolution.

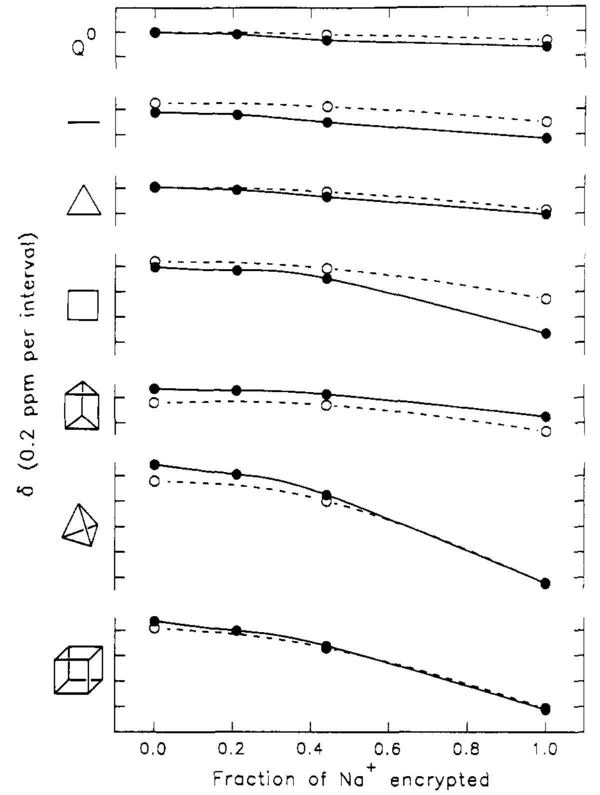

Figure 6. Dependence of ^{29}Si chemical shifts on the fraction of encrypted Na^+ ions in the solutions of Figure 5.[20] Closed symbols and solid lines correspond to measurements at 274 K, and open symbols and broken lines to those at 298 K. All shifts are referenced to the monomer Q^0 resonance of the solution containing no cryptand.

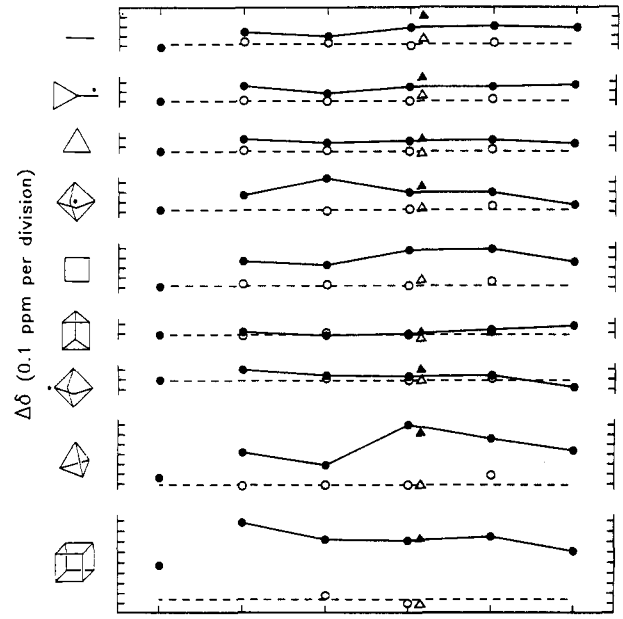

Figure 7. ^{29}Si chemical shifts, relative to the monomer resonance, for the solutions described in Figures 2 and 3.[20] Closed symbols and solid lines correspond to solutions with nonencrypted cations, and open symbols and broken lines to those with fully encrypted cations. Solutions c and d in Figure 2, i.e. those to which Cl^- was added, are represented by symbols ▲ and △, respectively.

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(28) Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979.

Conclusions

Three means are evident by which alkali-metal cations influence aqueous silicate equilibria. First, electrostrictive water-structuring by small cations increases the overall level of polymerization. This effect is probably significant only with lithium. Second, polymerization is increased further owing to silicate–M^+ ion-pairing. Cations promote encounters between dissolved silicate anions by overcoming their electrostatic repulsion. Because strongly paired cations will resist subsequent formation of a siloxane bond, the extent of polymerization increases as in the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ (i.e., as ion-pair formation constants decrease). Third, ion-paired cations stabilize several specific oligomers by immobilizing labile appendages and large ring structures.

Acknowledgment. Early discussions with Drs. J.-M. Lehn and T. W. Swaddle are gratefully acknowledged. We thank the Lakehead University Senate Research Committee and the Natural Sciences and Engineering Research Council of Canada for financial assistance.